

# THERMODYNAMIC INVESTIGATION OF THE LIQUID Pb-Bi ALLOYS AT 848°K

By

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DEPARTMENT OF METALLURGICAL ENGINEERING

INDIAN INSTITUTE OF TECHNOLOGY KANPUR

AUGUST, 1975

# **THERMODYNAMIC INVESTIGATION OF THE LIQUID Pb-Bi ALLOYS AT 848°K**

A Thesis Submitted  
in partial Fulfilment of the Requirements  
for the Degree of  
**MASTER OF TECHNOLOGY**

By  
**RAMESH CHANDRA AGARWALA**

to the

**DEPARTMENT OF METALLURGICAL ENGINEERING**  
**INDIAN INSTITUTE OF TECHNOLOGY KANPUR**  
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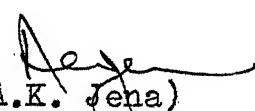
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CERTIFICATE

This is to certify that the work 'THERMODYNAMIC INVESTIGATION OF THE LIQUID Pb-Bi ALLOYS AT 848°K', has been carried out by Mr. Ramesh Chandra Agarwala under my supervision and that it has not been submitted elsewhere for a degree.

  
(A.K. Jena)

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POST GRADUATE OFFICE  
This thesis has been approved  
for the award of the Degree of  
Master of Technology (M.Tech.)  
in accordance with the  
regulations of the Indian  
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## CHAPTER - I

### INTRODUCTION

The advantage of thermochemical calculations is that the vast number of equilibria encountered in metallurgical processes may be computed from a much smaller number of functions characteristic of the separate compounds or elements which take part. These functions can be determined more easily than the equilibrium constants. Thermodynamic properties of liquid alloys are useful for the purpose of extraction, refining, alloy making etc.

The present work on Lead-Bismuth was undertaken because of the importance of low melting liquid alloys in reactors for conduction and in other nuclear engineering applications. Also available thermodynamic data on the Pb-Bi system do not seem to be consistent with the phase diagram.

## CHAPTER - II

### REVIEW OF LITERATURE

#### 2.1 Various Methods<sup>(1,2)</sup>

In one of the methods the vapour pressure of one of the components of the alloy is measured as a function of composition. Many experimental methods have been recently developed for this purpose. It is possible to calculate various thermodynamic properties from this data. Though the results of the evaporation studies have yielded much useful thermodynamic information it is not sufficiently reproducible to provide much information concerning the structure and nature of the bonding in the surfaces of solid materials.

The calorimetric technique measures the changes in the enthalpy or heat content of substance, associated with changes in temperature, changes of states such as melting and boiling, changes of chemical combination such as reactions and alloying, dissolution or changes of physical structure, annealing, recovery and grain growth etc. But it is not possible to measure heats of reaction at low temperatures directly. The energy change of interest may have to be obtained as the small difference between two large quantities with the consequent need for high precision

in the measurement. These methods measure the total energy difference between two states and kinetic studies are therefore tedious.

The well-known three electrochemical techniques are the ones which use the aqueous, molten and solid electrolytes for the determination of the thermodynamic quantities. Because of the evaporation of electrolyte at working temperatures the scope of the former one is limited. For high temperatures solid electrolytes are most convenient. But many systems can not be investigated with solid electrolyte particularly at low temperatures as the electrolyte must have a minimum conductivity of  $10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$  which is only achieved at elevated temperatures. Moreover its use is limited because of the appearance of the electronic conductivity under highly reducing conditions. The molten electrolyte technique has got the advantage that the required conducting ion may be brought into the neutral fused halides, oxides, acetates melts by dissolving small amounts of the salt or compound for the conducting ion in the suitable melt. By this technique the thermodynamic properties of binary, ternary, quarternary systems etc. intermetallic compounds, carbides, sulphides etc. can be studied.

## 2.2 The E.M.F. Technique

Theor.: It is possible to obtain the changes in free energy of a reaction by measuring the e.m.f. of a suitable galvanic cell where the reaction is made to occur electro-chemically<sup>(3)</sup>. Thus in the following chemical cell,



where MX is the electrolyte (an ionic conductor) and the electrodes M and X gives an e.m.f. This e.m.f. is related to the standard free energy of formation of MX by the expression

$$\Delta G_{MX}^{\circ} = - nEF$$

where all the components are in their standard states and n is the number of electrons transferred during the reaction, F is the Faraday constant and E is the e.m.f.. If one measures the e.m.f. as a function of temperature their enthalpy and entropy changes can also be estimated.

One of the most important information available by this technique is the activity of a component in a binary or a multicomponent system. The reversible cell of the following type can be constructed for this purpose

|                   |  |                                      |
|-------------------|--|--------------------------------------|
| Pure metal<br>(A) | Electrolyte<br>containing ions<br>of metal (A) | Solution of<br>metals (A)<br>and (B) |
|-------------------|--|--------------------------------------|

If one gm-atom of metal is transferred from pure metal to an alloy the amount of work done is,

$$RT \ln a_A = - nEF$$

And  $a_A$  can be found out. To obtain reliable thermodynamic data one must however arrange to have well defined experimental conditions. So the following points should be kept in mind.

1. All exchange reactions between the alloy and the electrolyte must be absent.
2. Atmosphere surrounding the cell must not take part in the reaction.
3. Diffusion in the alloy must be fast to maintain a homogeneous alloy electrode.
4. Electrolyte must be purely ionic.
5. The electrodes and the electrolytes used must be pure.
6. Reversibility of the cell must be established beyond doubt.

Actually there is no single criterion which establishes the reversibility of an electrolytic cell. But if the following points are satisfied by any cell we can assume the cell to be reversible.

i) The e.m.f. values obtained on heating and cooling coincides within the limits of experimental errors.

ii) There should be no attack apart from a slight etch on the electrodes and there should not be any detectable change in their surface compositions.

iii) The potentials measured by a null method were in themselves should be reversible.

iv) The side reaction should not be present. If any such reaction is present corrected values should be taken<sup>(4)</sup>.

Electrolyte: A large number of investigations have been carried out using the fused salt electrolyte<sup>(5-33,40-44)</sup>. An eutectic mixture of AgCl + KCl was used by Ölander<sup>(5)</sup>. Pure fused  $\text{Ag}_2(\text{NO}_3)_2$  and molten solution of AgCl was used by Watcher<sup>(6)</sup>. An eutectic mixture of KCl and LiCl and some amount of baser chlorides were used by a number of workers<sup>(7,12,14,16,19,20-23,26-30,32,33)</sup>. Molten equimolar mixture of KCl and NaCl with small amount of baser chlorides were used by Egan<sup>(21)</sup>, Pratt<sup>(8)</sup> and Seigle<sup>(15)</sup>. Molten equimolar solutions of AgCl<sub>x</sub> and NaCl<sub>x</sub> used by Hillert et al<sup>(10)</sup>. The mixture of KCl, NaCl, AlCl<sub>3</sub> were used by Wilder<sup>(11)</sup>. Mixture of LiCl and RbCl, sodium and potassium acetates were used by Ölander<sup>(13)</sup>. Eutectic mixture of LiBr and RbBr<sup>were used</sup> by Trunbore et al<sup>(25)</sup>.

Purification of Electrolyte: Metallic sodium was added to the electrolyte by Kleppa<sup>(12)</sup> to reduce oxidation of metal due to the traces of H<sub>2</sub>O present. Ölander<sup>(13)</sup> added CdCl<sub>2</sub> and Cadmium acetate to the electrolyte. Oriani<sup>(11)</sup> added RbCl. Seigle<sup>(15)</sup> had added .2 mole pct. of FeCl<sub>2</sub> and .5 mole pct. of NH<sub>4</sub>Cl. Fused KOH was added to neutralise the Hydrogen ions which might have formed from hydrolysis of moisture in the salt by Chipman and Elliott<sup>(19)</sup> and Taylor<sup>(20)</sup>. NH<sub>4</sub>Cl was added by Melgren<sup>(32)</sup> for preventing hydrolysis. For the same reason Trunbore et al<sup>(25)</sup> added NH<sub>4</sub>Br.

Wagner<sup>(34)</sup> heated the mixture of LiCl, KCl and CdCl<sub>2</sub> with NH<sub>4</sub>Cl at 350°C until all NH<sub>4</sub>Cl was vapourised. He also melted LiCl, KCl, SnCl<sub>2</sub> under stream of purified HCl and subsequently in purified N<sub>2</sub>. Rosenthal et al<sup>(31)</sup> dehydrated the electrolyte under vacuum at 150°C before placing it in the shell and the final dehydration was affected by the application of moderate heat at 10<sup>-3</sup> mm of Hg. Elliott and Chipman<sup>(19)</sup> melted KCl, LiCl at 400°C, added fused KOH and small amount of Cadmium pellets and then the temperature was raised to 500°C. After one hour the temperature was lowered to 400°C. The electrolyte was finally filtered through pyrex glass wool. Hillert et al<sup>(10)</sup> purified the electrolyte by electrolysis at 350°C for 24-36 hours with 2 V between graphite electrodes under an

atmosphere of dried argon. Laitinen et al<sup>(35)</sup> evacuated the mixture of LiCl, KCl at .15 to .2 mm Hg for 6 hours. Then ground it to a fine powder by ball mill. Evacuated this for 3 days and raised the temperature to 300°C in 8 hours. The temperature was again raised to 500°C, HCl was passed, the cell was evacuated and it was filled with argon. The cell was again evacuated and filled with argon. Gardner et al<sup>(36)</sup> ground the fresh chlorides to ASTM 30 mesh, heated to 100°C under vacuum and then raised the temperature to 500°C. These chlorides were mixed in a dry box and transferred to the cell. Salomons et al<sup>(37)</sup> carried out similar process as Gardner et al<sup>(36)</sup> and in addition to it they treated the mixture with HCl and evacuated for a long time. Oriani<sup>(7)</sup> prepared equimolar mixture of KCl, LiCl and some amount of AgCl and CuCl in separate container by holding at 500°C in contact with pure Ag or Cu wire for atleast 3 days under vacuum of about 1  $\mu$  Hg. Meanwhile the cell itself was prepared by holding it under the same vacuum at a temperature above the melting point of the alloy. The electrolyte was forced in to the cell by pure helium. Pratt<sup>(8)</sup> dehydrated the equimolar mixture of KCl, NaCl by prolonged heating under vacuum. The mixture of alkali halides with some NH<sub>4</sub>Cl was loaded in to a recrystallized alumina crucible and placed in a continuously evacuated and heated silica chamber. The

temperature was progressively raised from 200°C to 660°C in 7 days. .1 mole pct. of AgCl which had been similarly dehydrated at 200°C was added to the molten salt. Kleppa<sup>(12)</sup> melted LiCl and KCl in a cell and degassed by heating for sometime at 600-650°C. Metallic sodium was treated with it in molten state. Oriani<sup>(14)</sup> took KCl and LiCl in an auxiliary container and held at 400°C in contact with pure Cu wire under constant evacuation for 4 days. Some amount of RbCl was added to attain lower temperatures without freezing of the electrolyte. Melgren<sup>(32)</sup> dehydrated KCl and LiCl separately at 230-250°C in 24 hours. NH<sub>4</sub>Cl was added which decomposed to HCl and NH<sub>3</sub>. The salt mixture was melted in an argon atmosphere and heated slowly to 600°C.

Electrodes: The solid electrodes were used by a number of people<sup>(5-10,14,15,25,28,32)</sup>. The electrodes in the liquid form were used by a number of workers<sup>(11-13,16-19,21-24,26,29-31,33)</sup>.

Ölander<sup>(5)</sup> prepared alloys from .999 Au and .99975 Ag. Electrodes used by Oriani<sup>(7,14)</sup> were 99.99 pct. pure. Pratt<sup>(8)</sup> used 99.99 pct. pure Ag and 99.95 pct. Pd. Wilder<sup>(11)</sup> used 99.999 pct. components. Kleppa<sup>(12)</sup> used Bi containing .03 pct. Au and Tl containing .007 pct. Au. Ölander<sup>(13)</sup> used components pure up to .9999. Kleppa<sup>(18)</sup>

used Sn containing less than .04 pct. Pb, less than .01 pct. Fe, less than .004 pct. Cu and Sb, less than .002 pct. Bi. Au used was 99.9 pct. pure. Chipman and Elliott<sup>(19)</sup> used Pb in amounts equal to .001 of atom fraction of Sb in case of Cd-Sb alloys. Strickler and Seltz<sup>(22)</sup> used metals purified electrolytically, the Pb being plated from Bett's<sup>(38)</sup> bath and Bi by a method described by Swift<sup>(39)</sup>. Seltz and Dunkerley<sup>(23)</sup> used chemically pure Sn containing less than .01 pct. of impurities. Trunbore et al<sup>(25)</sup> used samples free of metallic impurities within .02 to .05 pct. Seltz et al<sup>(26)</sup> used commercially pure Cd containing less than .005 pct. impurities. Rosenthal<sup>(31)</sup> used Pb 99.9995 pct. pure and Zn 99.999 pct.

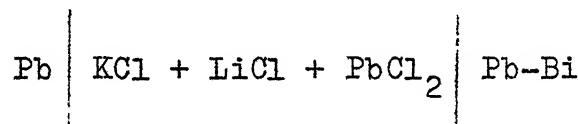
E.M.F. Measurements: The lead wires used for measuring the e.m.f. was Ag welded with Cu wires<sup>(5,8)</sup>. A number of investigators used W lead wires<sup>(7,12,16-20,23,24,32,33)</sup>. Hillert et al<sup>(10)</sup> used Al protected by quartz tubes. Wilder<sup>(11)</sup> and Egan<sup>(21)</sup> used Ta lead wires. Oriani<sup>(28)</sup> used Pt suspension wires which were Ag soldered with W wires. Hildebrand and Sharma<sup>(30)</sup> soldered W wires with heavy Au wires.

Reproducibility of measurements have been reported to be  $\pm .01$  mV<sup>(17,10)</sup>,  $\pm 0.02$  mV<sup>(26)</sup>,  $\pm 0.05$  mV<sup>(19,30)</sup>,  $\pm .1$  mV<sup>(5,6,9,17,33)</sup>,  $\pm 0.2$  mV<sup>(17)</sup>,  $\pm 0.3$  mV<sup>(24)</sup> and  $\pm .5$  mV<sup>(12)</sup>.

Temperature Measurements: For temperature measurements chromel-alumel<sup>(5,6,11,17,19,21,30)</sup>, iron constantan<sup>(22)</sup> and Pt-Pt, Rh (10 pct.)<sup>(7,31)</sup> thermocouple have been used. The temperature ranges used for the e.m.f. measurements are shown in Table 2.1.

### 2.3 The Pb-Bi System

The Pb-Bi alloys can be used to form a cell of the type given below:



The difference in the standard free energy of formation of chlorides of the components in the binary system investigated by the e.m.f. techniques are shown in Table 2.1.

At  $500^{\circ}\text{C}$   $\Delta G^{\circ}$  of formation of  $\text{PbCl}_2$  from its components<sup>(3)</sup> is -58 Kcal/mole and for  $\text{BiCl}_3$ , -38 Kcal/mole. Since the difference of  $\Delta G^{\circ}$  is 20 Kcal/mole which is quite appreciable amount, this cell is feasible. (Table 2.1)

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Table 2.1  
Temperature Ranges and  $\Delta (\Delta G^\circ)^\oplus$  for Chlorides

| System | Components whose activity is measured | Range of temperature °K | $\Delta (\Delta G^\circ) \text{ Kcal}$ for chlorides | Reference |
|--------|---------------------------------------|-------------------------|--|-----------|
| Ag-Pd  | $x_{\text{Pd}} = .1-.95$              | 1000                    |  | 8         |
| Ag-Sb  | $x_{\text{Sb}} = .322-.622$           | 478-648                 | 0.5  | 41        |
| Ag-Sb  | $x_{\text{Sb}} = .024-.316$           | 673-773                 | 0.5  | 42        |
| Ag-Sn  | $x_{\text{Sn}} = .3-.9$               | 900                     | 20.0   | 9         |
| Ag-Sn  | $x_{\text{Sn}} = .86-.994$            | 608-686                 | 20.0   | 11        |
| Ag-Zn  | $x_{\text{Zn}} = .28-.82$             | 773-873                 | 35.0   | 43        |
| Al-Zn  | $x_{\text{Zn}} = .05-.9$              | 560-820                 | 49.5   | 10        |
| Au-Cd  | $x_{\text{Cd}} = .56-.99$             | 520-580                 | 74.0   | 13        |
| Au-Cd  | $x_{\text{Cd}} = .16-.76$             | 640-870                 | 74.0   | 13        |
| Au-Cu  | $x_{\text{Cu}} = .42-.78$             | 620-760                 | 47.0   | 14        |
| Au-Cu  | $x_{\text{Cu}} = .15-.85$             | 120-131                 | 47.0   | 7         |
| Au-Tl  | $x_{\text{Tl}} = .8-.9$               | 723-1023                |  | 12        |
| Au-Sn  | $x_{\text{Sn}} = .22-.9$              | 773-873                 | 35.0   | 18        |
| Bi-Cd  | $x_{\text{Cd}} = .1-.95$              | 673-873                 | 30.0   | 19        |
| Bi-Cd  | $x_{\text{Cd}} = .25-.85$             | 683-748                 | 30.0   | 32        |
| Bi-Cd  | $x_{\text{Cd}} = .164-.857$           | 695-1123                | 30.0   | 20        |
| Bi-Mg  | $x_{\text{Mg}} = .1-.85$              | 763-1123                | 89.0   | 21        |
| Bi-Pb  | $x_{\text{Pb}} = .005-.95$            | 392-743                 | 23.0   | 22        |
| Bi-Sn  | $x_{\text{Sn}} = .10-.89$             | 608                     | 20.5   | 23        |

Continued...

Table 2.1 continued.

|       |                       |          |       |    |
|-------|-----------------------|----------|-------|----|
| Bi-Zn | $X_{Zn} = .064-.974$  | 692-923  | 35.50 | 24 |
| Cd-Pb | $X_{Pb} = .063-.89$   | 648-873  | 7.0   | 19 |
| Cd-Pb | $X_{Pb} = .214-.871$  | 700-845  | 7.0   | 20 |
| Cd-Sb | $X_{Sb} = .519-.858$  | 648-823  | 30.0  | 19 |
| Cd-Sb | $X_{Sb} = .104-.6556$ | 643-788  | 30.0  | 26 |
| Cd-Sn | $X_{Sn} = .05-.9$     | 648-893  | 9.5   | 19 |
| Cd-Sn | $X_{Sn} = .15-.75$    | 773      | 9.5   | 32 |
| Cd-Sn | $X_{Sn} = .15-.9$     | 703-858  | 9.5   | 20 |
| Cd-Sn | $X_{Sn} = .18-.92$    | 633-713  | 9.5   | 27 |
| Co-Pt | $X_{Pt} = .27-.68$    | 970-1181 |       | 28 |
| Pb-Sb | $X_{Sb} = .1-.31$     | 700      | 23.0  | 33 |
| Pb-Sb | $X_{Sb} = .13-.84$    | 643-903  | 23.0  | 29 |
| Pb-Sn | $X_{Sn} = .33-.67$    | 773      | 0.5   | 33 |
| Pb-Sn | $X_{Sn} = .91-.99$    | 683-823  | 0.5   | 44 |
| Pb-Zn | $X_{Zn} = .04-.99$    | 692-923  | 12.5  | 24 |
| Pb-Zn | $X_{Zn} = .04-.99$    | 873      | 12.5  | 31 |
| Sb-Sn | $X_{Sn} = .1-.9$      | 905      | 20.5  | 9  |
| Sb-Sn | $X_{Sn} = .86-.92$    | 685      | 20.5  | 17 |
| Sb-Zn | $X_{Zn} = .15-.92$    | 753-893  | 25.0  | 29 |
| Sn-Zn | $X_{Zn} = .14-.85$    | 704-843  | 15.0  | 20 |

\* Values are taken from reference (3).

## CHAPTER - III

### EQUIPMENT AND PROCEDURE

#### 3.1 Furnace and Temperature Control

A non-inductive nichrome wound tube furnace of 40 ohms resistance was used. The furnace was 60 cms long and 57 mm I.D. The winding was in the middle 35 cms of the furnace tube. 20 cms of the furnace tube was closed at the bottom by a refractory brick. A bottom closed chromium plated nickel tube of 0.5 mm thickness and 20 cms length was placed inside the furnace and earthed to avoid pickup of any induced e.m.f. as well as to homogenise the furnace temperature. A Leeds and Northrup temperature controller was used. A 20 ohms resistance was connected to the relay of the controller such that in the off position about 60 pct. of the current was allowed to pass through the furnace. A 36 gauge chromel-alumel thermocouple was placed between the nickel jacket and the furnace tube and connected to the controller. The cold junction of the thermocouple was placed inside ice-water bath. In this way the temperature of the furnace was controlled to  $\pm 2^{\circ}\text{C}$  for a period of 24 hours.

### 3.2 Design and Fabrication of Cell

The cell was made in a quartz crucible of 45 mm O.D. and 10 cms height. The crucible had a optically flat bottom and two small holes at the top. This crucible rested on quartz beads placed at the bottom of another quartz tube of 50 mm O.D. and 50 cms long. The quartz tube was used so as to be able to evacuate the system at high temperatures. The outside quartz tube had a B-60 high vacuum ground quartz joint attached to the open end. This tube was closed by a B-60 high vacuum ground pyrex joint. The pyrex joint was connected to a closed end 50 mm O.D. pyrex tube. This tube had two side tubes at  $180^{\circ}$  apart for inlet and outlet of argon gas. The outlet side tube carried a two-way stop cock and extended 20 cms inside the cell as shown in figure 3.1. So as to prevent short circuiting of gas flow. The inlet side was connected to a three way stop cock through a ground glass joint to have connections to the vacuum pump and the gas line. Four tubes of 12 mm diameter were connected on the top of the 50 mm O.D. pyrex tube. Each of these 4 tubes were joined to 6 mm pyrex tubes by using O-ring joints. Figure 3.1 shows the details of the cell. The B-60 joint was prevented from

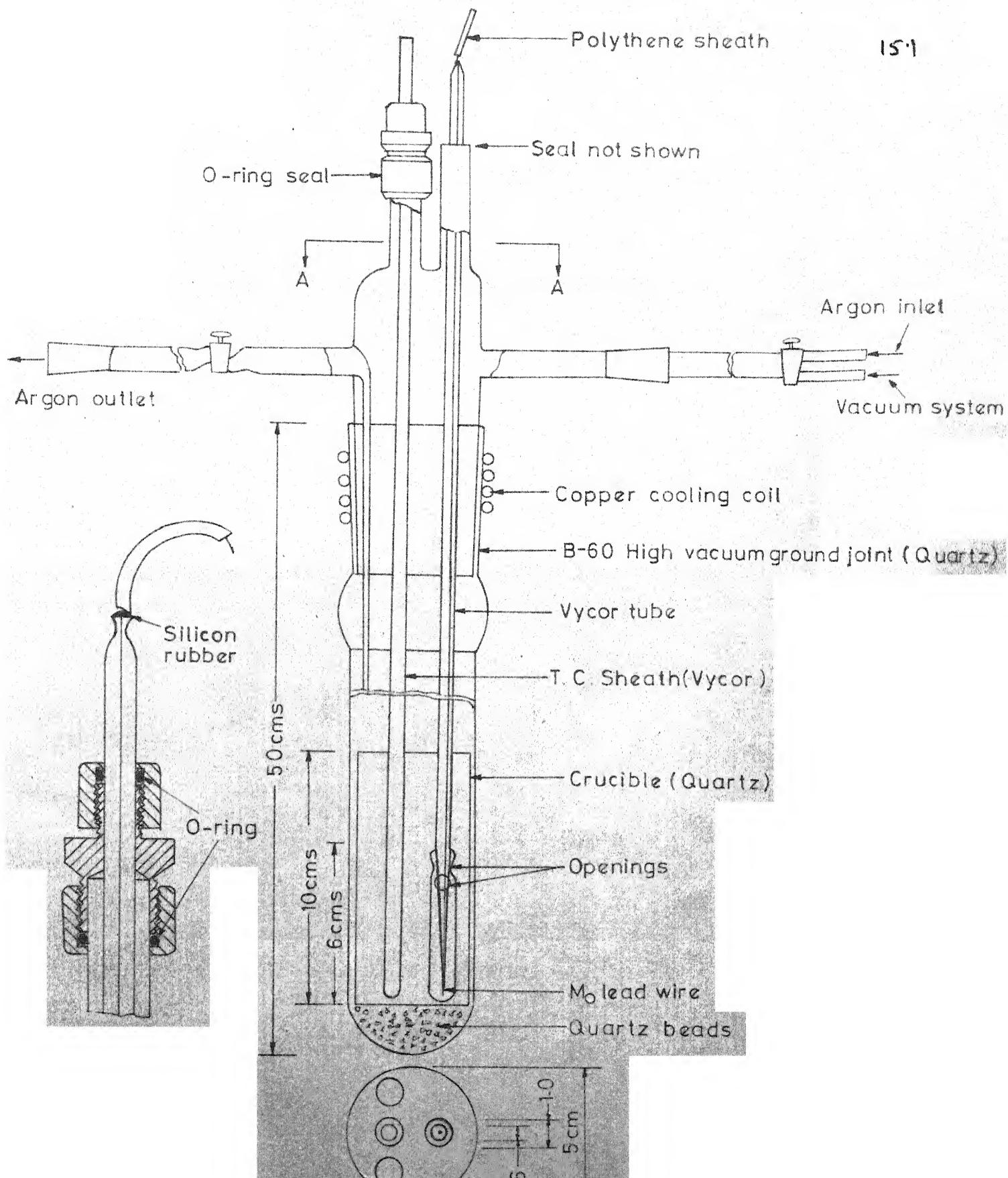


FIG. 3.1 CELL ASSEMBLY

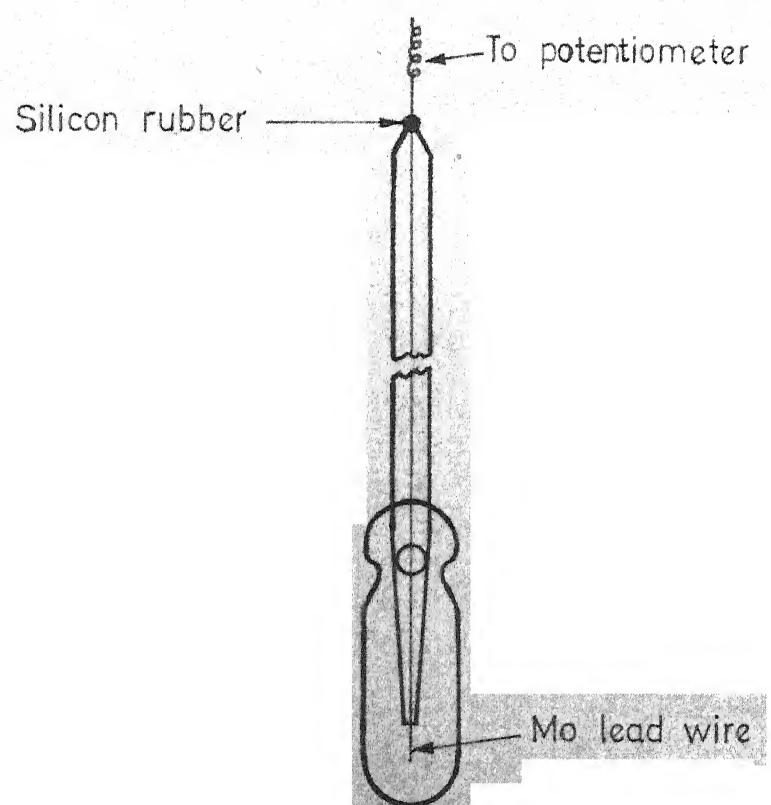


Fig. 3.2 The Electrode

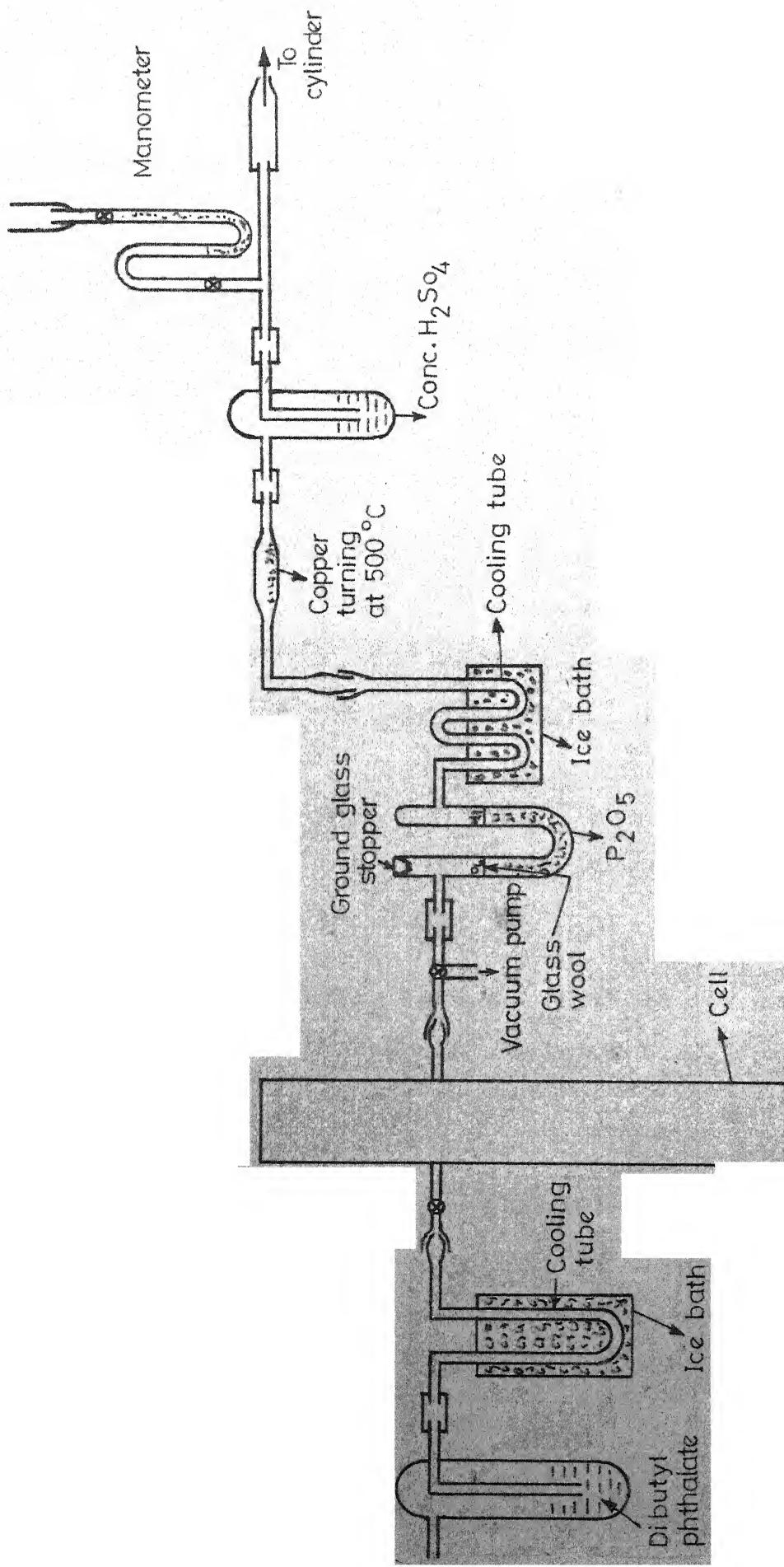


Fig. 3.3 Gas Purification Train

getting heated up by circulating water through a 6.5 mm diameter Cu tube wound around the joints.

The electrodes as shown in figure 3.2 were made of 6 mm O.D. Vycor tubes of 75 cms length. At one end of this tube was attached another Vycor tube of 2.5 mm diameter and 4 cms length. 1 mm diameter well annealed and <sup>wires</sup> cleaned molybdenum/were sealed inside these tubes. The wire projected about 3 mm at the tip of the 2.5 mm diameter tube. This tip was covered by a bulb of 6 cms length and 9.5 mm O.D. The bulb had 4 holes so that the alloys can be put inside and the electrolyte can get inside the bulb. The other end of the 6 mm Vycor tube was sealed under vacuum with silicon rubber.

### 3.3 Purification of Gas

The argon used was purified for oxygen and moisture by passing it through concentrated  $H_2SO_4$ , oxygen free copper turning heated to  $500^{\circ}C$  and then passing it through  $P_2O_5$ . The details of the gas purification train is shown in figure 3.3. A U-tube manometer containing dibutyl phthalate was introduced into the system, so as to be able to fill the evacuated cell with argon properly.

The gas coming out of the cell was cooled in a U-tube kept in a ice-bath and bubbled out in a bubbler containing dibutyl phthalate.

### 3.4 Vacuum System

The vacuum system used consists of a diffusion pump backed by a rotary pump of model VS - 4 supplied by Hindhivac Company. The assembly contains a liquid nitrogen trap and a  $P_2O_5$  trap to protect the oil from contamination.

### 3.5 Temperature and E.M.F. Measuring Unit

A type K-4 potentiometer with a d.c. galvanometer manufactured by Leeds and Northrup were used to measure the e.m.f. of the cell. The potentiometer is capable of measuring 0.5 microvolts in the range of 0.16 volts.

The 36 gauge chromel and alumel wires were first annealed by passing a current at 40 volts. The homogeneity of wires was tested by measuring the e.m.f. across a wire when it is pulled through liquid nitrogen. The length of wire showing constant e.m.f. was selected for making the thermocouple. This wire was twisted and the bead was made by striking arc with a mercury bath kept under kerosene at 40 volts. The hot junction of the thermocouple was passed through a 6 mm diameter Vycor tube closed at the bottom. The thermocouple tube was pushed inside the cell through a O-ring joint at the top of the cell. The cold junction was made by soldering 18 gauge enamelled Cu-wires using a  $ZnCl_2$  flux and it was kept in a ice-water bath.

For measuring the e.m.f. of the cell the molybdenum lead wire were connected to 18 gauge enamelled Cu-wires by Cu-connectors. The copper and molybdenum lead wires were covered with polythene sleeves to protect them from draught. These wires were fixed on stands so as to protect them from moving and picking up stray e.m.f.

### 3.6 Experimental Procedure

3.6.1 Cleaning of the apparatus: The whole glass apparatus was first cleaned by chromic acid care was taken to avoid contact of chromic acid with the ground joints by applying ample amount of grease on the joints. The apparatus was then cleaned with alcohol followed by distilled water. Finally it was cleaned with demineralised water and assembled inside the furnace for drying at  $120^{\circ}\text{C}$  for a period of 24 hours. After drying, the cell was flushed with argon for 2 hours to ensure complete removal of moisture.

3.6.2 Preparation of the electrolyte: The electrolyte was prepared using AR grade of  $\text{LiCl}\cdot\text{H}_2\text{O}$ ,  $\text{KCl}$  and  $\text{PbCl}_2$  of the following purity:

|                             |  |                   |
|-----------------------------|--|-------------------|
| KCl                         | $\text{LiCl} \cdot \text{H}_2\text{O}$ | $\text{PbCl}_2$   |
| Free acid (as HCl) 0.0018   | Sulphate 0.04                          | Pure for analysis |
| <b>Free alkali (as KOH)</b> | <b>As 0.0001</b>                       |                   |
| 0.0028                      | Fe 0.002                               |                   |
| Al 0.001                    | Pb 0.001                               |                   |
| As 0.00004                  |  |                   |
| Ba 0.001                    |  |                   |
| Bromide and Iodide 0.005    |  |                   |
| Ca 0.001                    |  |                   |
| Chlorate 0.003              |  |                   |
| Heavy metals (as Pb)        |  |                   |
| 0.0005                      |  |                   |
| Mg 0.0005                   |  |                   |
| Phosphate 0.001             |  |                   |
| Na 0.02                     |  |                   |
| Sulphate 0.001              |  |                   |
| Nitrogen 0.001              |  |                   |

Since the LiCl-KCl eutectic mixture cannot be effectively dehydrated by vacuum, the salts were dried separately by the following process. Appropriate amounts of  $\text{LiCl} \cdot \text{H}_2\text{O}$ , KCl and  $\text{PbCl}_2$  were weighed to give approximately 104 cc of molten electrolyte. The volume of the molten electrolyte was determined by melting appropriate amounts of the salts in a separate 45 mm diameter pyrex crucible outside the cell. Three tubes of diameter 12 mm and 18 mm with optically flat bottoms and having holes at the other end

were placed inside the crucible. These tubes were filled with KCl and  $\text{PbCl}_2$ . LiCl was put in the crucible. wires Molybdenum/were attached to the holes in the tubes containing KCl and  $\text{PbCl}_2$ . The crucible was lowered into the main quartz tube with the help of threads which passed through the holes in the crucible. The main cell was closed, all the O-ring joints were tightened and the vacuum pump was attached to the system.

When evacuation of the cell was started a lot of moisture started coming out. In order to protect the pumps the vacuum system was connected to the cell through a liquid nitrogen trap. The cell was evacuated at room temperature for 24 hours. It was then slowly heated to  $40^\circ\text{C}$  and evacuated for 8 hours. The vacuum obtained in this much of time was only 50 microns because of slow process of moisture evolution. The cell was now attached to diffusion pump. With the help of a liquid nitrogen trap the cell was evacuated to  $1.5 \times 10^{-6}$  mm Hg. This vacuum was maintained for about 8 hours. To ensure complete removal of moisture the cell was slowly heated in steps of  $5^\circ\text{C}$  to reach  $120^\circ\text{C}$  in 6 hours while heating only the backing pump was used. At  $120^\circ\text{C}$  the cell was evacuated to  $1.5 \times 10^{-6}$  mm of Hg and maintained for 6 hours. The temperature was increased slowly in steps of  $5^\circ\text{C}$  to  $150^\circ\text{C}$  in 7 hours. At  $150^\circ\text{C}$  the cell was evacuated to  $1.5 \times 10^{-6}$

mm of Hg for 12 hours to ensure complete removal of moisture. Now the temperature was raised to 500°C at a rate of 25°C per hour while the backing pump was operating. At 500°C the cell was evacuated at  $1.5 \times 10^{-6}$  mm of Hg for 16 hours. Now argon was flushed at 500°C for 15 minutes and the cell was evacuated immediately to  $1.5 \times 10^{-6}$  mm of Hg for 12 hours to remove any moisture carried by argon from rubber tube connections. Now argon was flushed and the temperature was lowered to 400°C. The joint was opened while a torch of argon was kept on the top of the cell. Now the tubes containing KCl and PbCl<sub>2</sub> were taken out with the help of Mo wires allowing the dry KCl and PbCl<sub>2</sub> powder to fall into the crucible containing LiCl. The cell was closed and evacuated. This operation took a few minutes. After evacuation for 2 hours at  $1.5 \times 10^{-6}$  mm of Hg argon was flushed for 15 minutes and the cell was again evacuated for an hour. Argon was introduced into the cell and the temperature was raised to 575°C. A positive pressure was maintained by the flow of argon. The electrolyte was not ready for experimentation.

**3.6.3 Preparation of electrodes:** The lead and bismuth used for the preparation of alloys were 99.999 pct. pure. Appropriate amounts of lead and bismuth were weighed on an electronic balance to give 0.1, 0.3, 0.5, 0.7 and 0.9 mole fraction of lead in the alloy. The metals were sealed

under vacuum in a quartz tube and held  $150^{\circ}\text{C}$  above the liquidus temperature for 4 hours. The alloy was taken out by breaking the quartz tube and the process was repeated to ensure homogenisation of the alloy. The alloy was taken out and crushed to a powder of 1 mm particle size, and kept in a dessicator. The tips of molybdenum wires inside the bulbs of electrodes were cleaned by electrolysing in a concentrated NaOH solution<sup>(19)</sup> at 2 Volt d.c. at 3.5 Amps/cm<sup>2</sup> current density. The molybdenum-wire was the anode and a stainless steel wire was the cathode. The molybdenum tip was then washed with alcohol and dried.

3.6.4 Measurement of e.m.f.: When the electrodes and the electrolyte were ready the outlet stop cock of the cell was closed, the O-ring joints were made loose, the 6 mm blind tubes were taken out and the electrodes were inserted inside the cell chamber. They were kept over the crucible in the temperature range of  $500^{\circ}\text{C}$ . The O-ring joints were tightened and argon flow was stopped. The cell was evacuated for an hour. Argon was introduced into the cell and a positive pressure was maintained inside the cell. The electrodes were slowly rotated and pushed inside the crucible containing electrolyte. The molybdenum lead wires were connected to the potentiometer and the e.m.f. readings were taken. It took about 8-12 hours. The temperature was then raised to  $600^{\circ}\text{C}$  and was brought back

575°C. The e.m.f. was noted again as a function of time until it was constant. It took about a couple of hours. Now the temperature was lowered to 550°C and was again brought back to 575°C. The e.m.f. was noted again until it was constant, again. The values of the e.m.f. reported in Chapter - IV are the average e.m.f. values of the three e.m.f. readings. When the e.m.f. readings were taken the temperature of the cell was read simultaneously with the help of another potentiometer.

## CHAPTER - IV

### RESULTS

#### 4.1 The Partial Molar Free Energy and Activity of Lead

The measured e.m.f. values at 848°K for compositions 0.1, 0.3, 0.5, 0.7 and 0.9 mole fractions of lead are tabulated in Table 4.1. The partial molar free energy of lead in lead-bismuth alloys are obtained directly from the e.m.f. given in Table 4.1 by using the equation,

$$\Delta \bar{G}_{Pb} = - nFE$$

where

$\Delta G_{Pb}$  = The partial molar free energy of lead related to liquid lead in cal/mole

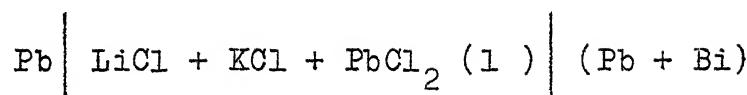
n = 2, since for Pb  $\rightarrow$  Pb<sup>++</sup> the valence change

F' = 23061 cal/Volt equivalent

$\Delta \bar{G}_{Pb}$  values are listed in Table 4.1. The activity of lead in the alloy is related with  $\Delta \bar{G}_{Pb}$  by the equation,

$$\Delta \bar{G}_{Pb} = RT \ln a_{Pb} \quad (4.1)$$

The values of activity of Pb are calculated with the help of equation 4.1 using experimental  $\Delta \bar{G}_{Pb}$  values and are also listed in Table 4.1.

Table 4.1 E.m.f. obtained with the cellat  $848^{\circ}\text{K}$ 

| Composition of<br>the alloy,<br>$x_{\text{Pb}}$ | e.m.f. (Volts)           | $\Delta \bar{G}_{\text{Pb}}$<br>cal/mole | $a_{\text{Pb}}$ |
|---|--------------------------|--|-----------------|
| 0.1   | $0.114,000 \pm 0.00050$  | -5,260                                   | 0.045           |
| 0.3   | $0.051,000 \pm 0.00025$  | -2,355                                   | 0.245           |
| 0.5   | $0.032,000 \pm 0.00010$  | -1,475                                   | 0.420           |
| 0.7   | $0.016,150 \pm 0.000050$ | -745                                     | 0.645           |
| 0.9   | $0.003,749 \pm 0.000030$ | -175                                     | 0.900           |

## 2.2 Partial Molar Free Energy of the Pb-Bi Alloys

It is convenient to employ the excess partial molar properties for this analysis. Denoting the excess properties by the superscript 'ex' the partial molar excess free energy is defined by the following equation

$$\Delta \bar{G}_{\text{Pb}}^{\text{ex}} = \Delta \bar{G}_{\text{Pb}} - RT \ln X_{\text{Pb}} \quad (4.2)$$

$\Delta \bar{G}_{\text{Pb}}^{\text{ex}}$  values are obtained from the data in Table 4.1.

In order to obtain the excess free energies of Bi from those of  $\Delta \bar{G}_{\text{Pb}}^{\text{ex}}$  the following, <sup>form</sup> of Gibb's-Duhem equation is to be evaluated,<sup>(3)</sup>

$$\Delta \bar{G}_{\text{Bi}, X_{\text{Bi}}}^{\text{ex}} = - \alpha_{\text{Pb}} X_{\text{Pb}} X_{\text{Bi}} - \int_{X_{\text{Bi}}=1}^{X_{\text{Bi}}} \alpha_{\text{Pb}} dX_{\text{Bi}} \quad (4.3)$$

where,

$$\alpha_{\text{Pb}} = \frac{\Delta \bar{G}_{\text{Pb}}^{\text{ex}}}{(1 - X_{\text{Pb}})^2}$$

The  $\alpha_{\text{Pb}}$  values were plotted as a function of  $X_{\text{Bi}}$  and a smooth curve was passed through the experimental points.  $\Delta \bar{G}_{\text{Pb}}^{\text{ex}}$  values at compositions 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8 and 0.9 mole fractions of lead in the alloy were obtained from  $\alpha_{\text{Pb}}$  values at these compositions.

$\Delta \bar{G}_{\text{Bi}}^{\text{ex}}$  values were obtained from the area of the  $\alpha_{\text{Pb}} - X_{\text{Bi}}$

plot using equation 4.3. These partial molar quantities at 848°K for the lead component and bismuth component are listed in Table 4.2 and 4.3 respectively. From the  $\Delta \bar{G}^{\text{ex}}$  values the  $\Delta \bar{G}$  values were calculated using equation 4.2. These values are listed in Tables 4.2 and 4.3. The activity of components are calculated by equation (4.1). The activity coefficient which is given by  $\gamma = a/X$  are also calculated. The values of activity and activity coefficients are listed in Table 4.2 and Table 4.3.

The partial molar free energies are plotted in figure 4.1 and the partial molar excess free energies are plotted in figure 4.2. The activities and activity coefficients are plotted in figure 4.3. All these figures show expected and consistent behaviour of the alloys.

#### 4.3 Integral Molar Properties

The integral molar properties are obtained from the partial molar properties by the equation like

$$\Delta G = X_{\text{Pb}} \Delta \bar{G}_{\text{Pb}} + X_{\text{Bi}} \Delta \bar{G}_{\text{Bi}} \quad (4.4)$$

Using this relation  $\Delta G^{\text{ex}}$  and  $\Delta G$  values are obtained, and listed in Table 4.4. They are also plotted in figures 4.1 and 4.2 showing consistent behaviour.

Table 4.2 Partial molar properties of lead in liquid alloys at 848°K

| $X_{Pb}$ | $a_{Pb}$ | $\gamma_{Pb}$ | $\Delta \bar{G}_{Pb}$<br>cal/mole | $\Delta \bar{G}_{Pb}^{ex}$<br>cal/mole |
|----------|----------|---------------|-----------------------------------|--|
| 0.0      | 0.0      | (0.25)        | - ∞                               | (-2200)                                |
| 0.1      | 0.045    | 0.450         | -5,260                            | -1,380                                 |
| 0.2      | 0.130    | 0.650         | -3,420                            | -710                                   |
| 0.3      | 0.245    | 0.815         | -2,355                            | -325                                   |
| 0.4      | 0.330    | 0.825         | -1.855                            | -310                                   |
| 0.5      | 0.420    | 0.840         | -1.475                            | -305                                   |
| 0.6      | 0.520    | 0.865         | -1,105                            | -245                                   |
| 0.7      | 0.645    | 0.920         | -745                              | -145                                   |
| 0.8      | 0.775    | 0.970         | -430                              | -52                                    |
| 0.9      | 0.900    | 1.000         | -175                              | +3                                     |
| 1.0      | 1.000    | 1.000         | 0                                 | 0                                      |

Table 4.3 Partial molar properties of  
bismuth in liquid Pb-Bi  
alloys at 848°K

| $x_{Bi}$ | $a_{Bi}$ | $\gamma_{Bi}$ | $\Delta \bar{G}_{Bi}$<br>cal/mole | $\Delta \bar{G}_{Bi}^{ex}$<br>cal/mole |
|----------|----------|---------------|-----------------------------------|--|
| 0.0      | 0.000    | (0.38)        | - $\infty$                        | (-1060)                                |
| 0.1      | 0.050    | 0.50          | -5015                             | -1135                                  |
| 0.2      | 0.115    | 0.58          | -3645                             | -935                                   |
| 0.3      | 0.215    | 0.72          | -2580                             | -555                                   |
| 0.4      | 0.320    | 0.80          | -1910                             | -365                                   |
| 0.5      | 0.420    | 0.85          | -1455                             | -285                                   |
| 0.6      | 0.510    | 0.86          | -1145                             | -285                                   |
| 0.7      | 0.600    | 0.86          | -880                              | -270                                   |
| 0.8      | 0.730    | 0.91          | -530                              | -155                                   |
| 0.9      | 0.880    | 0.98          | -220                              | -40                                    |
| 1.0      | 1.000    | 1.00          | 0                                 | 0                                      |

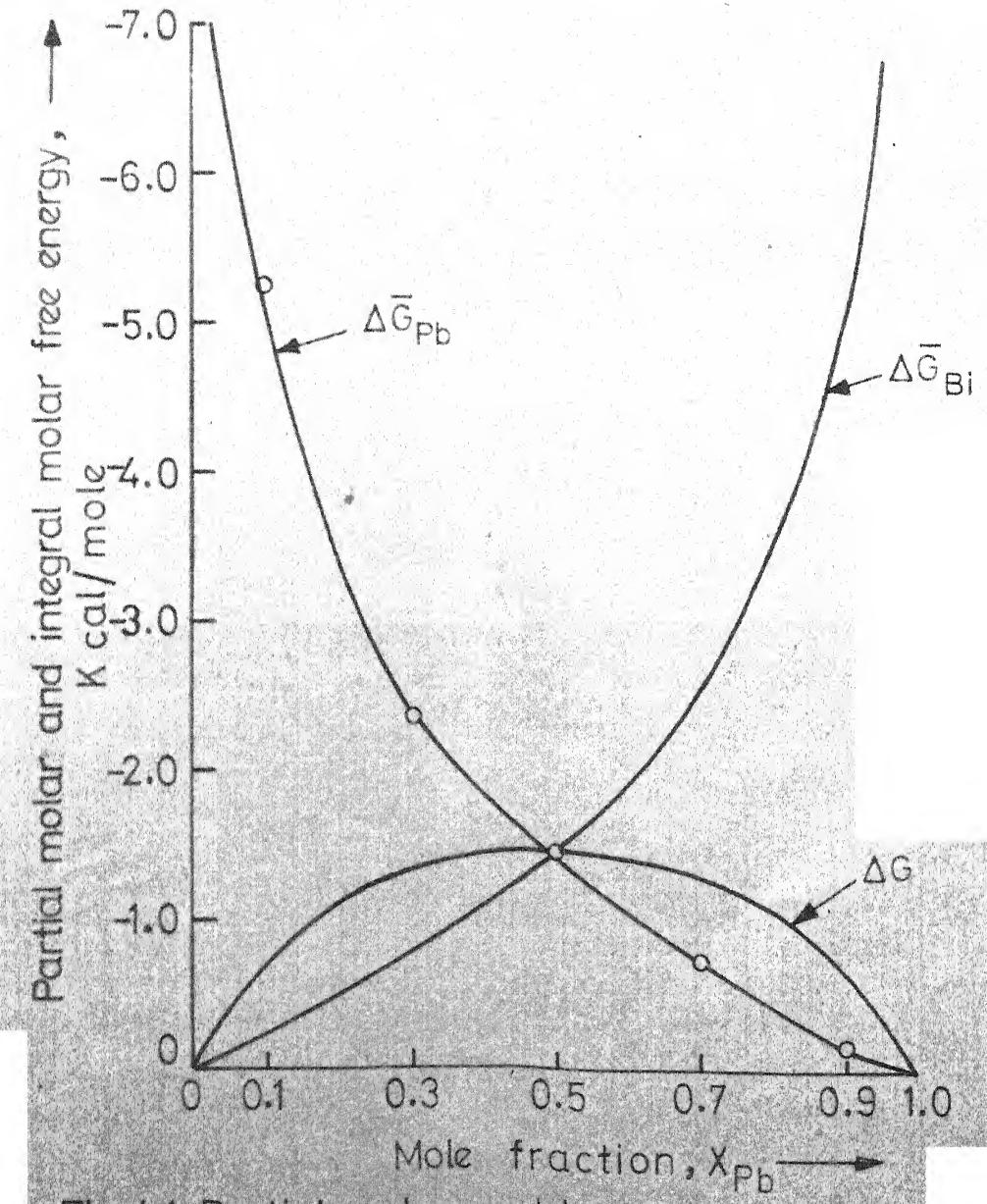


Fig.4.1 Partial molar and integral molar free energies of the Pb - Bi alloys at 848 °K

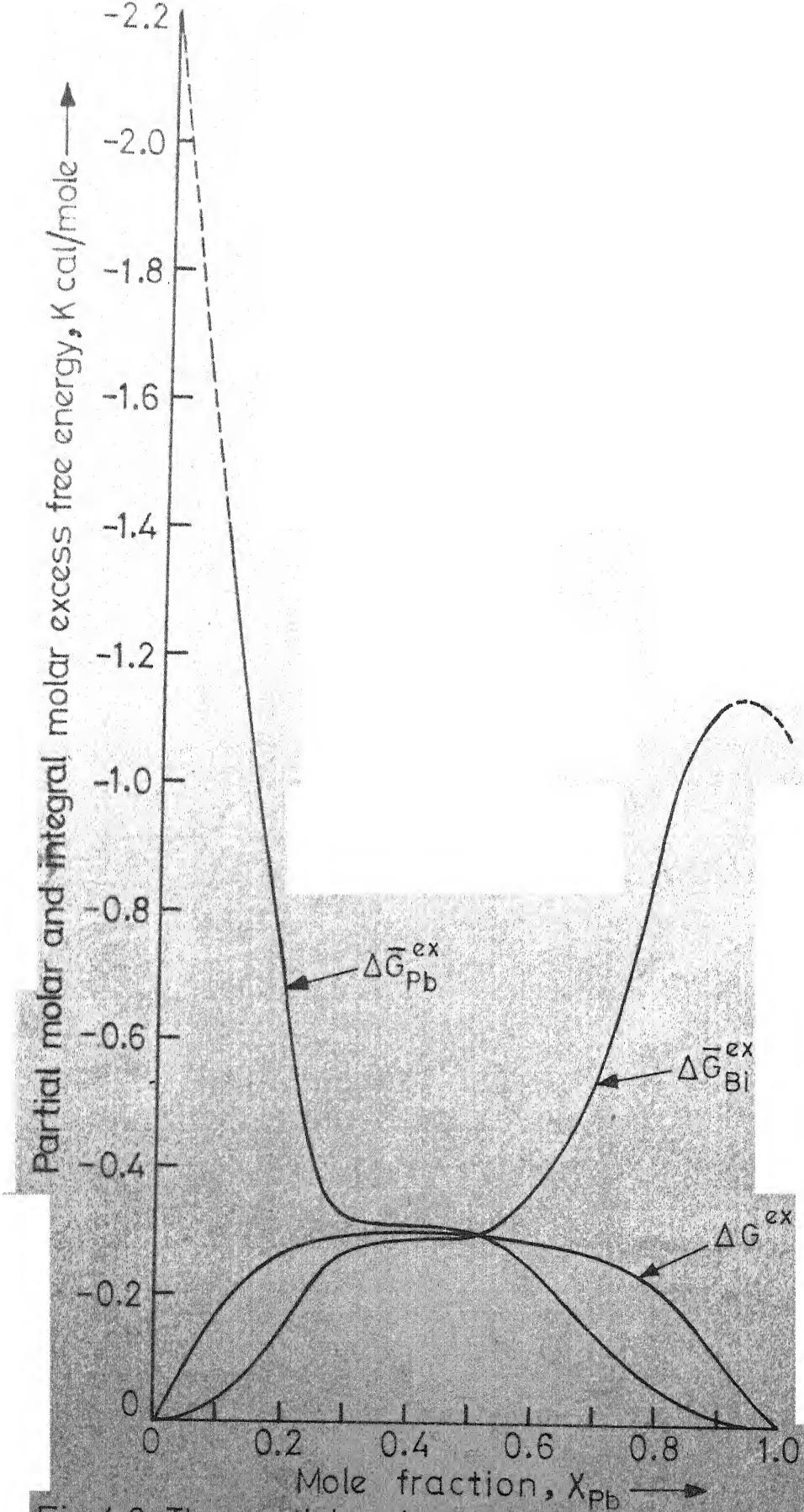


Fig.4.2 The partial molar and integral molar excess free energies of Pb-Bi alloys at 848 °K

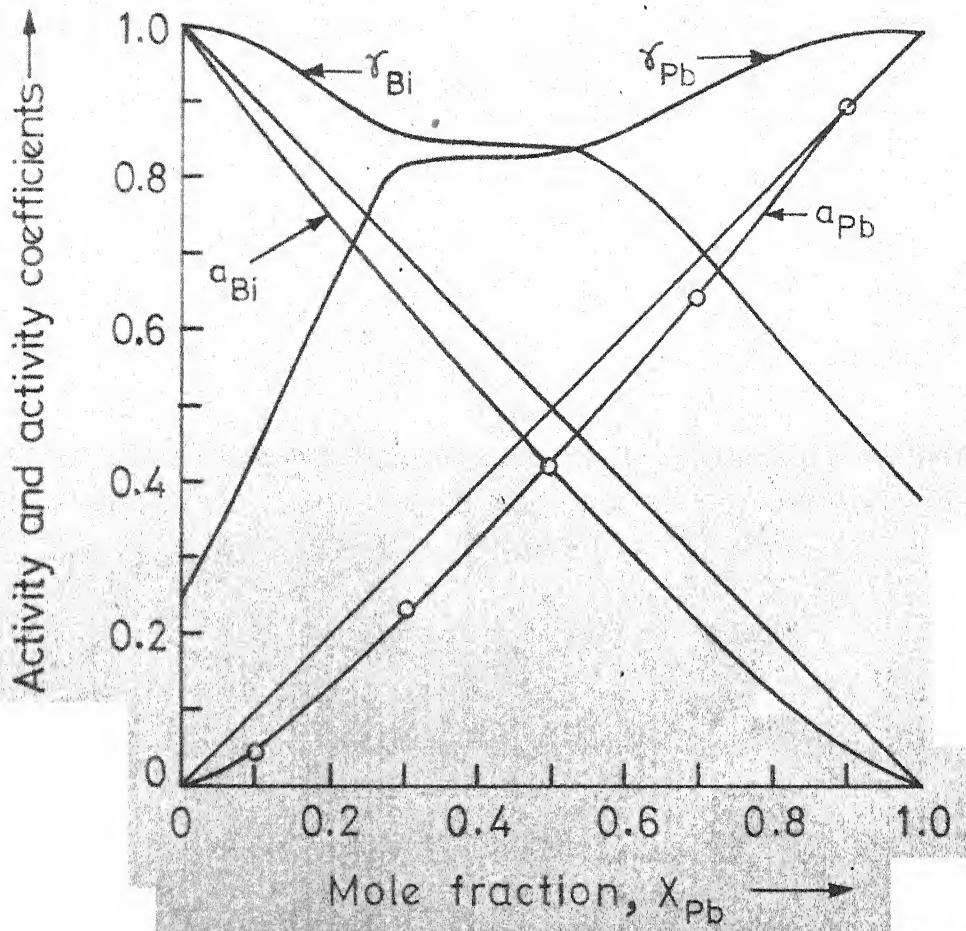


Fig. 4.3 Activity and activity coefficients of the components in the Pb-Bi alloys at 848 °K

Table 4.4 Integral molar properties of liquid Pb-Bi alloys at 848°K

| $x_{Pb}$ | $x_{Bi}$ | $\Delta G$<br>cal/mole | $\Delta H^\theta$<br>cal/mole | $\Delta S$<br>cal/mole<br>-deg | $\Delta G^{ex}$<br>cal/mole | $\Delta S^{ex}$<br>cal/mole<br>deg |
|----------|----------|------------------------|-------------------------------|--------------------------------|-----------------------------|------------------------------------|
| 0.1      | 0.9      | -725                   | -80                           | 0.761                          | -175                        | 0.12                               |
| 0.2      | 0.8      | -1110                  | -155                          | 1.126                          | -265                        | 0.13                               |
| 0.3      | 0.7      | -1320                  | -210                          | 1.309                          | -290                        | 0.10                               |
| 0.4      | 0.6      | -1430                  | -245                          | 1.397                          | -295                        | 0.06                               |
| 0.5      | 0.5      | -1465                  | -250                          | 1.433                          | -295                        | 0.05                               |
| 0.6      | 0.4      | -1430                  | -235                          | 1.409                          | -290                        | 0.07                               |
| 0.7      | 0.3      | -1295                  | -205                          | 1.285                          | -270                        | 0.07                               |
| 0.8      | 0.2      | -1075                  | -150                          | 1.091                          | -225                        | 0.09                               |
| 0.9      | 0.1      | -660                   | -80                           | 0.684                          | -110                        | 0.04                               |

\*  $\Delta H$  values are taken from reference (45).

A number of investigators<sup>(33,22,40)</sup> in the past have obtained  $\Delta H$  values from the temperature coefficients of e.m.f. However these data are not reliable and differ appreciably from the calorimetric data.<sup>(45,46)</sup> Kleppa<sup>(45)</sup> has determined  $\Delta H$  values<sup>at</sup>  $623^{\circ}\text{K}$  and  $723^{\circ}\text{K}$ . His results suggest that  $\Delta H$  is independent of temperature therefore his  $\Delta H$  values are accepted and are listed in Table 4.4. From our values of  $\Delta G$  and  $\Delta H$  the values of  $\Delta S$  and  $\Delta S^{\text{ex}}$  have been calculated and listed in Table 4.4. The  $\Delta S$  and  $\Delta S^{\text{ex}}$  values are plotted in figure 4.4 along with the values of  $\Delta S^{\text{id}}$ . The interesting manner in which  $\Delta S^{\text{ex}}$  varies in the system will be discussed later.

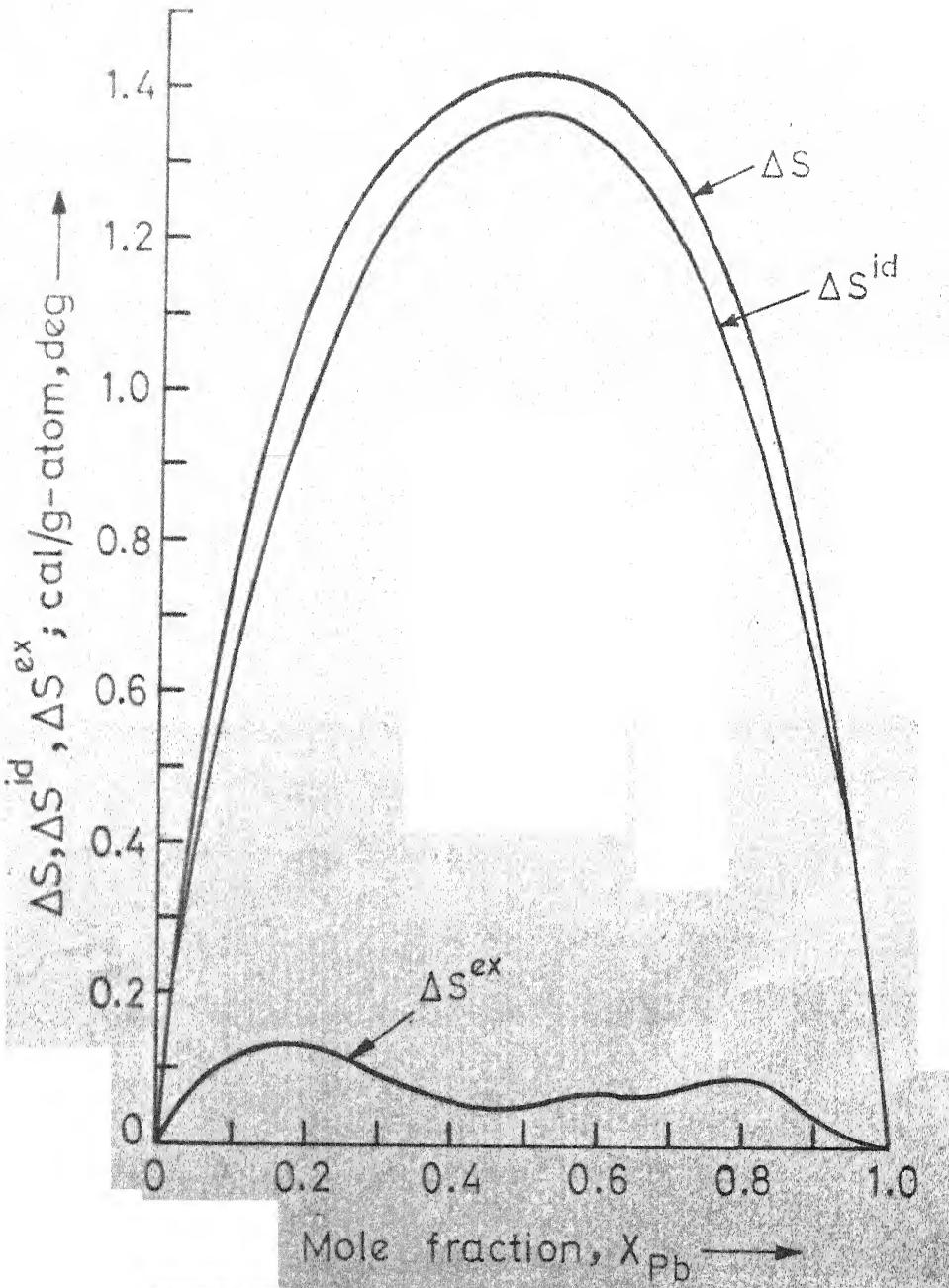


Fig.4.4 Entropy of formation, ideal entropy of formation and excess entropy of formation of Pb-Bi alloys at 848 °K

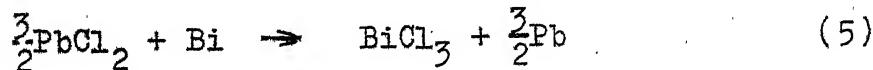
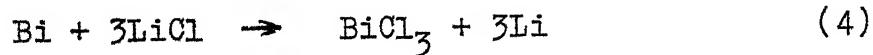
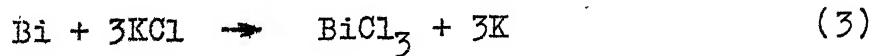
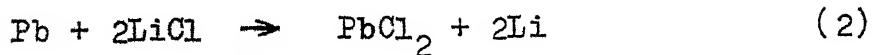
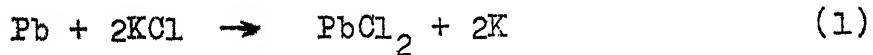
CHAPTER - V

## DISCUSSIONS

5.1 Sources of Errors

The various sources of errors which can hamper the functioning of the cell are discussed below.

Side reactions: During the study any reaction other than the one producing c.m.f. can give rise to errors. In the system studied the following are the possible side reactions whose thermodynamic feasibility was checked before commencing the experiment



On the basis of standard free energies of formation of chlorides<sup>(2,3)</sup> and assuming the equilibrium conditions the activities of Li, K and BiCl<sub>3</sub> were calculated. The calculated values are as follows

| <u>Reaction</u> | <u>Activity</u>               |
|-----------------|-------------------------------|
| 1               | $a_K \approx 10^{-27}$        |
| 2               | $a_{Li} \approx 10^{-23}$     |
| 3               | $a_{BiCl_3} \approx 10^{-71}$ |
| 4               | $a_{Li} \approx 10^{-70}$     |
| 5               | $a_{BiCl_3} \approx 10^{-14}$ |

The above values of activities suggest that these side reactions are negligible. The value of  $a_{BiCl_3}$  suggest the amount of  $BiCl_3$  in the electrolyte is very small. Also the activation energy for diffusion in liquid alloys is of the order of few kilo-calories. Therefore the alloy electrode composition is expected to remain unaltered after the experiment is completed. To avoid any moisture the cell was evacuated to a vacuum of  $10^{-6}$  mm Hg for about one day as described in Chapter III. Care was taken to prevent entrance of oxygen to the cell by purifying the argon gas and electrolysing the molybdenum lead wires. Also the gas train was flushed with argon before allowing it to pass through the cell to make sure that no oxygen enters the cell from rubber connections. Sufficient amount of (1 mol. wt%)  $PbCl_2$  was added to avoid reduction of  $PbCl_2$  by baser metals.

Stray e.m.f.: The stray e.m.fs. possible from furnace winding were avoided by having a non-inductive winding furnace. Stray e.m.fs. were further checked by placing a chrome-plated earthed nickel tube around the cell. During the course of e.m.f. measurement switching off the furnace did not alter the e.m.f. value. This ensured absence of stray e.m.f. due to furnace winding. The contact potentials of measuring unit were reduced by using earthed screened cables.

Cell reversibility: The basic requirement in the use of the equation  $\Delta \bar{G}_{Pb} = - nFE$  is that the cell is reversible. Reversibility can be inferred from the behaviour of the cell and the practical realization of this requirement in the cell studied was indicated by the following

- a) The constancy of e.m.fs. with time indicated no appreciable metal transfer
- b) The thermodynamic properties studied correlated well within themselves and a reasonable correlation with earlier studies.
- c) The constant values of e.m.f's obtained ~~after~~ at the temperature of study, disturbing the system to higher and lower temperatures and then bringing back to original temperatures

d) The available enthalpy values<sup>(48)</sup> suggest that a temperature variation of  $\pm 1^{\circ}\text{C}$  would have negligible effect on the e.m.f.

Ionic conduction: The cell must not have any electronic conduction. This arises at higher temperatures and from emulsion of metals in the electrolyte and impurities. Precautions have been taken to minimise this. Also the Pb-Bi system itself has very low vapour pressure which will prevent evaporation of metals. Evaporation changes the composition of alloy and causes electronic conduction.

## 5.2 Comparison With Other Data

The values of the  $\Delta \bar{G}_{\text{Pb}}$  obtained in present work is consistent with the  $\Delta \bar{G}_{\text{Pb}}$  values by the previous investigators<sup>(22,33,47)</sup>. The  $\Delta \bar{G}_{\text{Pb}}$  of present work along with those of Elliott et al<sup>(33)</sup> and Strickler<sup>(22)</sup> are plotted in figure 5.1. The figure shows that the  $\Delta \bar{G}_{\text{Pb}}$  values of both the previous works are very close to the present work. The data of Elliott et al<sup>(33)</sup> at  $773^{\circ}\text{K}$  are less negative than those reported in this investigation at  $848^{\circ}\text{K}$ . The results of Strickler et al<sup>(22)</sup> at  $700^{\circ}\text{K}$  are also less negative. Less negative values at lower temperatures are expected. Thus the present results compare well with the other data.

### 5.3 Internal Consistency of the Results

The internal consistency of the present results are confirmed by the following

- 1) From the figure 4.1 it is observed that  $a_{Pb}$ ,  $\Delta \bar{G}_{Pb}$ ,  $a_{Bi}$  and  $\Delta \bar{G}_{Bi}$  show smooth regular behaviour with composition
- 2) The  $\Delta \bar{G}_{Pb}$ ,  $\Delta \bar{G}_{Bi}$  values obtained by the same cell at  $823^{\circ}K^{(49)}$  are less negative than those obtained at  $848^{\circ}K$ .
- 3) The values of  $\Delta \bar{G}_{Pb}$  at  $848^{\circ}K$  calculated with the available  $\Delta H^{(45)}$  values and  $\Delta \bar{G}_{Pb}$  values at  $823^{\circ}K^{(49)}$  are in good agreement with those obtained experimentally at  $848^{\circ}K$ .

### 5.4 The Bonding in the Pb-Bi Alloys

The entropy of formation  $\Delta S$  is found to be more than the ideal entropy of formation. It means that other contributions apart from the configurational contributions are present which make  $\Delta S$  values greater than  $\Delta S^{id}$  values. It is expected to be the vibrational contribution which makes  $\Delta S$  more positive than  $\Delta S^{id}$ , because other contributions to  $\Delta S$  of Pb-Bi alloys are expected to be negligible. The excess entropy against composition curve shows two minima at  $X_{Pb} = 0.45$  and  $X_{Pb} = 0.65$ . At

these compositions the positive contribution to  $\Delta S$  appears to be less. The reason for it is likely to be either clustering or segregation in the alloy.

The phase diagram of Pb-Bi binary system (fig. 5.2) shows a eutectic around the composition  $X_{Pb} = 0.45$ . Which suggest that segregation in the liquid alloy of this composition may have been present. The phase diagram also shows the formation of a new phase at about  $X_{Pb} = 0.68$ . This again suggests association in the liquid state. It is thus postulated that in the Pb-Bi alloys the bonding is weaker which makes the  $\Delta S$  more positive than  $\Delta S^{id}$  and also there is association in the liquid state at around  $X_{Pb} = 0.65$  and segregation in the liquid state at around  $X_{Pb} = 0.45$ . This view is consistent with the experimental  $\Delta S^{ex}$  values and the phase diagram.

It may be noted that  $\Delta S^{ex}$  values obtained from the average free energy values<sup>(22,40)</sup> of the previous workers and the calorimetric heats of formation of Kleppa<sup>(45)</sup> do not seem to be consistent with the phase diagram.

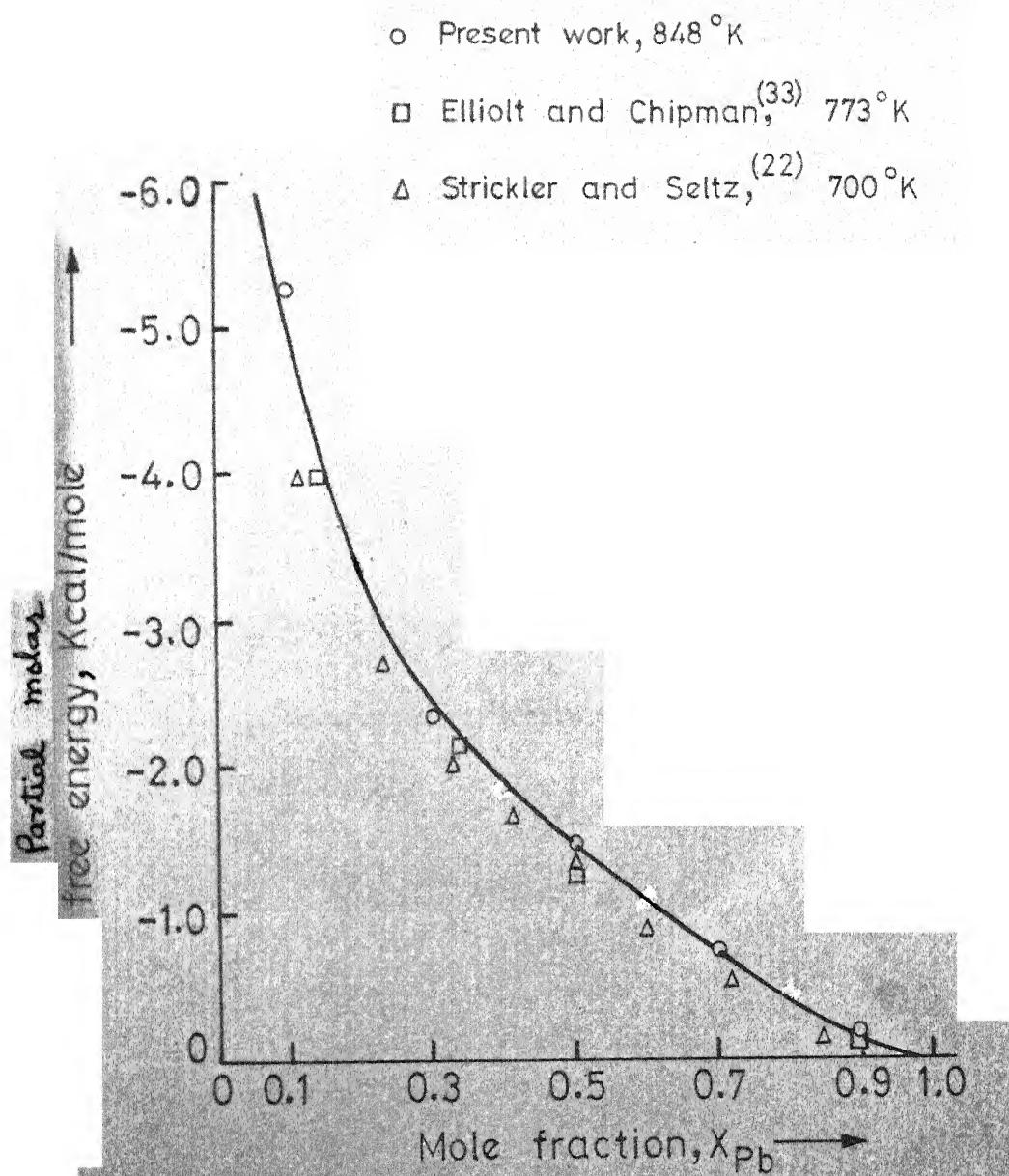


Fig.5.1 Experimental values of the partial molar free energies of lead in liquid Pb-Bi alloys

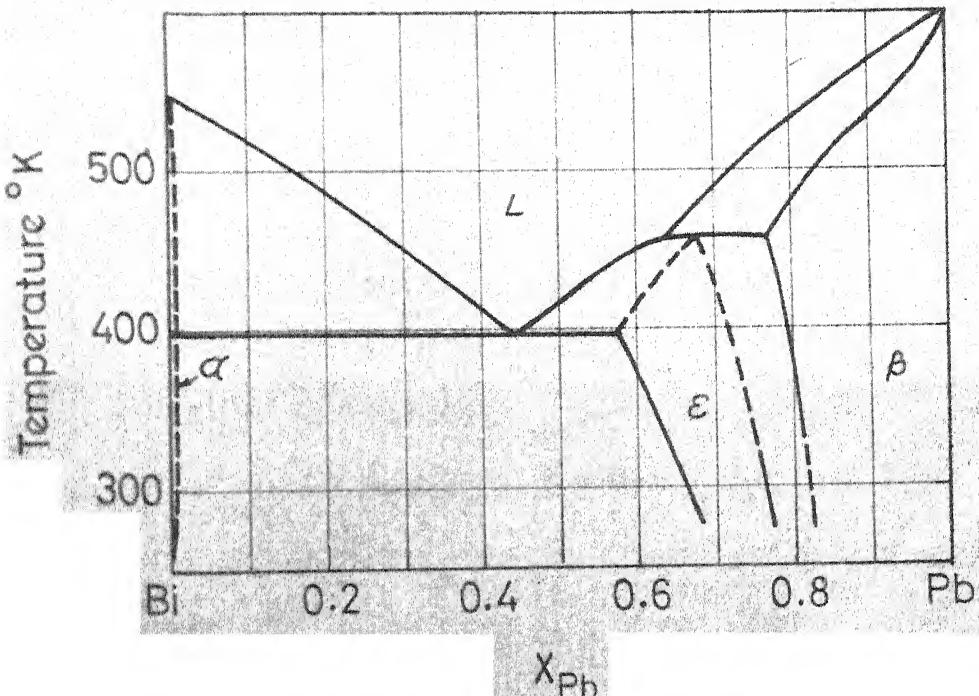
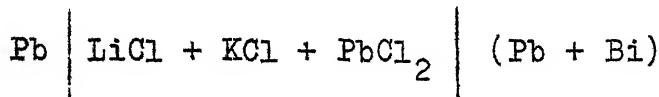


Fig. 5.2 Bismuth lead system

CHAPTER - VI

## SUMMARY AND CONCLUSIONS

1. Activities of lead in lead-bismuth alloys at 848°K are measured at various compositions i.e.  $X_{Pb} = 0.1, 0.3, 0.5, 0.7$  and  $0.9$  in the galvanic cell



2. Activity and activity coefficients of lead and bismuth partial molar and excess partial molar free energies of lead and bismuth are calculated and tabulated at  $X_{Pb} = 0.1$  to  $0.9$

3. By taking calorimetric  $\Delta H$  values<sup>(45)</sup>  $\Delta S$  and  $\Delta S^{ex}$  values are calculated and tabulated

4. All these thermodynamic functions are internally consistent and consistent with other published data.

5. The variation of  $\Delta S^{ex}$  with composition suggest that in the liquid alloy there is segregation at about  $X_{Pb} = 0.45$  and association at about  $X_{Pb} = 0.65$ .

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